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Heavy-Atom Kinetic Isotope Effects

An Indexed Bibliography

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

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Heavy-Atom Kinetic Isotope Effects

An Indexed Bibliography

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A necessary step in the operation of each of these data centers is the generation of comprehensive, thoroughly indexed bibliographies covering the fields of interest of the center. In most cases, these bibliographic files are computer-based. In the interest of making the full resources of the data centers of maximum utility to the scientific and technical community, selected bibliographies are published from time to time in the NBS Special Publication Series.

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David R. Lide, Jr., *Chief*
Office of Standard Reference Data

Contents

Heavy-Atom Kinetic Isotope Effects An Indexed Bibliography*

Marvin J. Stern and Max Wolfsberg*****

A bibliography of heavy-atom kinetic isotope effects has been compiled covering the complete literature from the earliest entry found (1911) through 1965. Review articles and theoretical papers are listed through 1968. The bibliography is divided into a list of the references, an author index and a subject index. The subject index has been annotated to describe, in brief, the type of reaction being observed. The following areas have been excluded: geochemistry (except for specific laboratory reactions), living systems, mass spectrometry and electron impact, electrochemistry, diffusion-controlled processes, hot-atom chemistry, photochemistry involving selective excitation of isotopes, and processes involving no chemical change.

Key words: Author index; bibliography; heavy-atom isotope effects; isotope effects; kinetic isotope effects; reaction kinetics; subject index.

Introduction

Background

The authors at first considered writing a critical review monograph on kinetic isotope effects. The literature embraced by this field was believed to be sufficiently large to be divisible into two parts: (1) isotope effects due to the substitution of hydrogen by deuterium or tritium; (2) isotope effects due to heavy-atom substitutions. To make the project manageable, only the latter aspect of the subject was chosen for the critical review.

However, after a bibliography containing approximately 500 references had been assembled, it was found that usually each experimental system was sufficiently different from the others to warrant separate analysis. In addition, the early papers contained many contradictory data which appeared to make critical analysis very difficult. As a consequence, the authors decided to reduce the scope of their effort and prepare an annotated index to the literature in the field. This endeavor has involved a thorough reading of the selected papers, and classification and indexing of the pertinent information. It is hoped that researchers engaged in kinetic isotope effect studies or others wanting to make use of such studies will find this indexed bibliography useful.

Description and Classification Scheme

The main, but by no means only, sources of pertinent references for the bibliography were Chemical Abstracts and Nuclear Science Abstracts through the year 1965. The search was extended through the year 1968, but only for review articles and theoretical papers. One review article published in 1969 is also included. The bibliography was checked against reprints in the files of the authors; references within the articles collected for the bibliography were checked for appropriateness of inclusion; and other appropriate bibliographies or partial bibliographies of the field were checked. Many of the authors' colleagues helped by submitting reprints of their articles. The papers finally included were generally restricted to those appearing in formally published literature (journal articles, chapters in books, proceedings of symposia, etc.). Thus, works such as doctoral theses, technical reports, and abstracts of talks presented at scientific meetings were, with rare exceptions, omitted. It is the belief of the authors that, for the period covered and topics considered (vide infra), the bibliography is better than 98 percent complete (except, perhaps, for Chinese literature). Articles that might have been missed probably fall into one of three categories: (1) papers published prior to 1966 but not appearing in the abstract journals until a later date; (2) reviews of reaction mechanisms containing very limited discussions of isotope effect studies; (3) papers on isotopic tracer studies which note only in passing the observation of kinetic isotope effects.

The study of the effect of isotopic substitution on a rate constant (kinetic isotope effect) serves to elucidate the reaction mechanism. There is strong interplay between experiment and theory in this area, and the experimental data are often interpreted by applying transition state theory (absolute reaction rate theory). The area of interest has been defined to include only in vitro reactions of well-defined reactants which are in thermal equilibrium. Isotope effects in the following areas have been specifically excluded: (1) geochemistry (unless the work involves specific labo-

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ratory reactions); (2) living systems; (3) mass spectrometry and electron impact; (4) electrochemistry; (5) diffusion-controlled processes; (6) processes not involving chemical change (with a few exceptions); (7) hot-atom chemistry; (8) photochemistry involving selective excitation of isotopes. General theoretical papers which have direct application to kinetic isotope effects have been included whether they deal specifically with heavy-atom effects or not. Some hydrogen isotope effect papers, which demonstrate points in kinetic isotope effect theory that have not been well-demonstrated by means of heavy-atom effects (e.g., unimolecular gas-phase reactions), have also been included.

The bibliography consists of three sections:

I. Listing of Papers
II. Author Index
III. Subject Index

The Listing of Papers contains the names of the authors, the titles of the papers, and the literature references. The reference abbreviations conform to the 1969 edition of ACCESS (Chemical Abstracts Service, American Chemical Society). The entries are arranged and numbered chronologically by years, and alphabetically according to authors' names within each year. The first entry is a paper by F. Soddy published in 1911. The listing numbers (total of 527) are used as references in the Author Index and Subject Index. The user can best acquaint himself with the Subject Index by skimming through it. Where appropriate, indexing is carried out by:

(1) isotope effect type, e.g., *Carbon-13 kinetic isotope effects;*

(2) common name of isotopically substituted reactant and reaction undergone, e.g., *Acetophenone (carbonyl-^{14}C) reaction with semicarbazide* [The *less-abundant* isotope in parentheses following the chemical name indicates the actual label or isotopic substitution considered. In the case of salts and esters, when the isotopic position is in the second part of the name (anion or acid moiety), the entry is repeated with the reactant name inverted; e.g., *Ethyl propionate (2-^{14}C)* . . . also appears as *Propionic acid (2-^{14}C), ethyl ester,* . . .];

(3) reaction type, e.g., *Decarboxylation reactions;*

(4) reaction name, e.g., *Diels—Alder reactions;*

(5) theoretical concepts, e.g., *Activation-energy effects* (The word "effects" without specification refers to effects on reaction kinetic isotope effects.);

(6) method employed, e.g., *Computer calculations of isotope effects.*

Purely theoretical articles and review articles are usually entered only once, under Theory or Reviews. On the average, there are five index entries per article. With relatively few exceptions, each paper was read for index entries by both of the authors. In general, under-listing was more feared than over-listing. If there was doubt about including a given entry in the index, it was usually included. Since the reading was carried out over a period of several years, some inconsistencies were introduced in the manner in which the papers were indexed. Although the authors have attempted to remove these inconsistencies in the final tabulation, some of them have undoubtedly been retained.

Inspection of the Subject Index makes for many interesting observations. For example, one sees that, among the heavy-atom kinetic isotope effects, carbon-13 and carbon-14 effects have been studied more than any of the others; among reaction types, decarboxylations have been the most studied.

The authors urge that the bibliography be updated at periodic intervals. Such a task will be easier than the present undertaking due to the fact that the indexing of isotope effects in Chemical Abstracts has been markedly improved during the past decade.

The authors wish to thank the Library staffs of the Belfer Graduate School of Science, Yeshiva University, and Brookhaven National Laboratory for their help and cooperation in the collection of articles appropriate for inclusion in the bibliography, as well as their many colleagues who sent them reprints of papers. Although the list of scientists who contributed in one way or another to the completion of this work is too long to present here, special acknowledgments are due Professor Takanobu Ishida for translating into English several Japanese articles, and Professors Irving J. Borowitz and Martin Pomerantz for answering scores of questions about organic chemistry, as well as for inspecting the final Subject Index for ambiguities. We are grateful to Dr. Marilyn L. Wolfsberg for help in reading proof. Finally, the authors wish to thank Professor Jacob Bigeleisen for suggesting that they undertake this project, and for his encouragement during the course of its development.

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II. Author Index

G

H

I

J

K

L

M

N

O

P

R

S

T

U

V

W

Y

Z

III. Subject Index

C

D

E

M

N

O

* Oxidation of labeled species.

P

Q

R

* Reduction of labeled species.

S

T

* Effects of isotopic substitution at several atomic positions measured for purposes of reaction-mechanism elucidation.

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A bibliography of heavy-atom kinetic isotope effects has been compiled covering the complete literature from the earliest entry found (1911) through 1965. Review articles and theoretical papers are listed through 1968. The bibliography is divided into a list of the references, an author index and a subject index. The subject index has been annotated to describe, in brief, the type of reaction being observed. The following areas have been excluded: geochemistry (except for specific laboratory reactions), living systems, mass spectrometry and electron impact, electrochemistry, diffusion-controlled processes, hot-atom chemistry, photochemistry involving selective excitation of isotopes and processes involving no chemical change.

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